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A STUDY OF POLYMERS
CONTAINING SILICON-NITROGEN BONDS ~~coll 2A~~

Progress Report 37 for the Period
February 4, 1964 to March 3, 1964

CRS 3331

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER
National Aeronautics and Space Administration
Huntsville, Alabama

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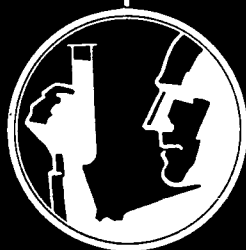
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Progress Report for the Period
February 4, 1964 to March 3, 1964

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER
National Aeronautics and Space Administration
Huntsville, Alabama

Project 1259, Report 37

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ABSTRACT

A

Attempts were made to develop a suitable calorimetric method for studying bond strengths in silicon-nitrogen compounds. Satisfactory combustion was not accomplished, and it now appears that others who have published data on silicon-oxygen and silicon-nitrogen bonds have had the same difficulty.

The reaction of silylamines with polyhydroxy compounds to form polymers was studied further. The reaction with ethylene glycol was encouraging in that it produced resilient polymers and coatings with fair thermal stability, but they require further evaluation. Reactions with pentaerythritol and phloroglucinol were not encouraging. The most interesting polymers were produced earlier with hydroquinone and p,p'-biphenol.

A tough coating 6-8 mils thick was prepared on aluminum from a methylphenyl silazane that was made in the presence of triethylamine. The coating remained undamaged while being heated at 400°C for 5 hours. Previously, no coatings of such thickness have endured comparable heating. The methylphenyl silazane-triethylamine product formed a resilient polymer when mixed with ethylenediamine silazane and cured in air. This resilient polymer was tougher than previous samples made without triethylamine, and it remained resilient after several hours in air at 400°C. These are further examples of the benefits of triethylamine in the reaction of amines with silicon halides.

Attempts to improve the strength of ethylenediamine as an elastomer were largely unsuccessful, but a possible improvement was made in its ability to plasticize other silazanes in coatings. The improvement was made by heating ethylenediamine silazane with bis(methylamino)diphenylsilane.

Improvements in the methods of curing silicon-nitrogen polymers with phenylene bridges have resulted in repetition of the earlier production of a tough elastomer. The schedule of heating while curing in air appears to be critical.

The influence of tertiary amines on the reaction of diphenyldichlorosilane with ammonia was studied in greater detail than before in an attempt to find a preferred reaction temperature. A reaction at 1-10°C gave about the same results as a reaction of 25-55°C. A reaction at 125-143°C was less successful in preventing cyclization. None of the reactions produced a high polymer.

A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

I. INTRODUCTION AND STATUS

Silicon-nitrogen compounds are being studied in an effort to produce thermally stable materials that will be useful in the space program. This report covers the eleventh month of the fourth year of the project.

Two types of elastomeric polymers are presently of principal interest. One, which is relatively weak but remains resilient after several hours at 400°C, was made from methylphenyldichlorosilane, ammonia, and triethylamine by mixing the reaction product with ethylenediamine silazane and curing it in air. The other elastomer was made from 1,4-bis(dimethylchlorosilyl)benzene by reaction with methylamine followed by curing in air. The second is much tougher than the first, but it remains resilient only about 30 minutes at 400°C.

Coating and adhesive agents for aluminum and stainless steel are also being investigated. A polymer recently made was applied to aluminum in a coating 6-8 mils thick, and it remained intact for 5 hours in air at 400°C.

Several different types of reactions are to be screened in the next month. An attempt is in progress to aminate phthalocyaninodichlorosilane as a route to a polymer. Also, reactions of silylamines with metaloxy compounds are being studied.

II. ATTEMPTS TO DETERMINE BOND STRENGTHS IN CYCLIC SILAZANE AND SILOXANE COMPOUNDS

A. Discussion

Attempts were made to determine bond strengths of silicon-nitrogen and silicon-oxygen bonds, because data in the literature do not explain the observed thermal stability of some of the silazane compounds. Calorimetric measurements of heats of combustion were attempted as a basis for calculating the silicon-oxygen and silicon-nitrogen bond strengths. The plan was to relate these bond strengths to the thermal stabilities of the siloxane and silazane compounds. However, it proved to be difficult to achieve complete combustion in a bomb calorimeter, and evidently previous investigators have had the same trouble.

Previous investigators found that during combustion in a bomb calorimeter, a crust of silica formed and protected part of the silicon compounds. Thompson,¹ in his thermochemical analysis of siloxane compounds, used benzoic acid as a promoter and found that it did not aid combustion; but he claims to have obtained complete combustion by a different technique in which he used two soft glass ampoules that were designed to explode at different time intervals during the burning. However, he admits that construction of glass ampoules that explode at the proper time is actually a matter of chance. Tanaka, et al² claim to have obtained complete combustion of some siloxane compounds by using glass ampoules to hold the sample. However, the heats of combustion measured by Tanaka are not in good agreement with measurements made by other investigators. Tanaka gives no indication of having detected crust formation in any of his calorimetric tests. Very little work has been done on the silazane compounds, and, therefore, comparison of the silicon-oxygen bond strength with the silicon-nitrogen bond strength is difficult. We attempted to develop a method of obtaining complete combustion of a cyclic silazane and a cyclic siloxane compound in an oxygen bomb.

-
1. Raymond Thompson, Journal of the Chemical Society, 1908 (1953).
 2. Toshio Tanaka, Ukiko Takahashi, Rokwro Okawara, and Takeo Watase, Journal of Chemical Physics 19, 1330 (1951).

In preliminary experiments intended to find a method of obtaining complete combustion, no attempt was made to make calorimetric measurements. Samples of hexamethylcyclotrisilazane, octamethylcyclotetrasiloxane, and solutions of each of these silicon compounds in highly combustible organic solvents were weighed in gelatin capsules; and the capsules were burned in an oxygen bomb. The silica crusts formed in these experiments indicated that the liquid samples would have to be distributed in some manner so that more surface area was exposed to oxygen for burning. Several different methods of providing more surface area were tried in efforts to obtain complete combustion. The methods tried were: spreading of the liquid sample in a thin film in a stainless-steel calorimeter pan, dispersal of the liquid on an asbestos-fiber mat, and creation of small liquid droplets completely exposed to oxygen. None of these methods resulted in complete combustion of the silicon compounds. A visual inspection of the oxygen bomb after each test indicated that the formation of a silica crust had prevented portions of the sample from burning. Calorimetric measurements were not attempted because an acceptable combustion method was not found. Obviously extensive effort would be required to find a means of improving combustion, and this amount of effort is not recommended at present.

B. Experimental Details

A commercial double-valve stainless steel oxygen bomb was used for the combustion tests. The bomb was charged with oxygen to a pressure of 25 atmospheres prior to each of the combustion tests. For ignition of the sample, a 34-gage Nichrome wire, 11 cm in length, was connected between the electrodes, and secured in position so that it touched the sample.

Hexamethylcyclotrisilazane and octamethylcyclotetrasiloxane were burned in the oxygen bomb as pure compounds and as mixtures with diethylether or benzene. The diethylether mixtures appeared to burn more completely than either the pure compounds or the benzene mixtures.

1. Combustion of the samples in gelatin capsules

Several samples of silazane and siloxane compounds were burned in thermally calibrated calorimeter capsules of gelatin. The gelatin capsules appeared to explode upon ignition and scatter the sample so that they aided in preventing the formation of a crust of silica. The crust that formed during the burning usually was in the form of thin flakes, and it was gray in color or speckled with black.

Hexamethylcyclotrisilazane, 0.3482 g, was burned in a gelatin capsule, and there was evidence of unburned carbon in the products. A 0.3692-g sample of octamethylcyclotetrasiloxane burned in a gelatin capsule also left products similar to those left after burning hexamethylcyclotrisilazane alone.

A 0.5762-g sample of a solution containing 51 weight per cent of diethylether and 49 weight per cent of hexamethylcyclotrisilazane in a gelatin capsule appeared to burn almost completely except for a small amount of gray residue directly under the capsule holder. Two other capsules containing diethylether and hexamethylcyclotrisilazane, with the ether in a slightly higher weight ratio, also burned with the same results. Two samples of mixtures of diethylether (51%) and octamethylcyclotetrasiloxane (49%) were also burned in the oxygen bomb. The smaller sample (0.3333 g) appeared to burn more completely than the larger sample (0.5270 g), but both combustions left some black soot in the areas beneath the capsules.

Mixtures of benzene with hexamethylcyclotrisilazane or octamethylcyclotetrasiloxane were tried. The benzene mixtures did not appear to burn as well as the diethylether mixtures, as indicated by much more pronounced crust formation. A 0.7767-g sample of a mixture of benzene (30%) and hexamethylcyclotrisilazane (70%) in a gelatin capsule formed a heavy crust of silica on burning. A 0.5913-g

sample of a 50% solution of hexamethylcyclotrisilazane in benzene formed a similar but less thick crust on burning, and there was evidence of unburned carbon in the crust. A 0.6013-g sample of a 49% solution of octamethylcyclotetrasiloxane in benzene burned with the formation of a heavy crust that appeared to be about the same as that formed on burning the sample of the 50% solution of hexamethylcyclotrisilazane in benzene.

2. Ignition of samples with more exposed surface area

Several different methods were tried for obtaining complete combustion. A very thin layer (0.2589 g) of pure hexamethylcyclotrisilazane was put in a stainless-steel calorimeter pan and burned in the oxygen bomb. A crust that contained unburned carbon was formed.

A 0.5134-g sample of a 46% solution of hexamethylcyclotrisilazane in diethylether was poured onto a mat of 0.0421 g of asbestos fibers, and the mixture was ignited. It appeared that combustion was less complete than in any of the bomb tests. The fibers obviously entrapped and shielded the ether solution so that silica crusts formed in the fibrous mass.

Since in all these bomb tests some incompletely oxidized material remained beneath the sample holder, an open-weave wire basket was designed to hold a gelatin capsule. A capsule containing 0.3192 g of a 46% solution of hexamethylcyclotrisilazane in diethylether was placed in the basket and ignited. Burning apparently was uneven, and portions of unburned capsule were found in the bomb after the burning.

III. REACTIONS OF SILYLAMINES WITH POLYHYDROXY COMPOUNDS

A. Discussion

The reaction of silylamines with polyhydroxy compounds to produce polymers has been studied further. Methylphenyl methylamino silazane, which is probably crude bis(methylamino)methylphenylsilane, was treated with several different hydroxy compounds with the results that are summarized below.

Reaction with pentaerythritol produced a yellow, sticky solid. Heating the solid at 190°C produced a fairly tough resilient solid that became very brittle in 30 minutes at 400°C. Because of this instability, further work with the product is not recommended at this time.

Reaction with phloroglucinol, 1,3,5-trihydroxybenzene, produced a rubbery material that became rigid and brittle in 10 minutes at 125°C. Hence phloroglucinol alone was not promising as a reactant with the silazane.

The reaction of the silazane with hydroquinone was described first in Report 35, page 22. The freshly prepared product softened at 100°C, but when held at 190°C for 96 hours, it was converted to a substance that was resilient at 100°C and rigid at room temperature. This result encouraged additional experiments to improve elastomeric properties. Phloroglucinol used with hydroquinone was expected to provide a means of cross-linking through the benzene rings, but it merely increased the embrittlement on heating. Incorporation of ethylenediamine silazane into the mixtures did not eliminate the trouble.

Three reactions were run with hexaphenylcyclotrisilazane and ethylene glycol in efforts to improve the elastic polymer that was described in Report 36, page 2. The initial experiments produced a soft elastic polymer with slow recovery time. When hexaphenylcyclotrisilazane was heated with 5% more than the stoichiometric amount of ethylene glycol, the results were similar to those previously reported. When a 5% excess of hexaphenylcyclotrisilazane was used, the product was softer, and it formed good coatings when cured on aluminum. In another experiment, a small amount of glycerol was added, and the product was a livelier, tougher elastomer. It was resilient after 30 minutes at 350°C, but 20 minutes at 400°C made it friable. Evaluation of the products of the reaction of hexaphenylcyclotrisilazane with ethylene glycol will be continued.

B. Experimental Details

Methylphenyl methylamino silazane was prepared by the reaction of methylphenyldichlorosilane with methylamine as described in Report 35, page 18. The purest distilled fraction was probably largely bis(methylamino)methylphenylsilane, and the molar weights below were calculated on that assumption.

1. Reaction of methylphenyl methylamino silazane with pentaerythritol

In a 50-ml, 3-neck flask equipped with dropping funnel, reflux condenser, thermometer, and magnetic stirrer were placed 3.4 g (0.025 mole) of pentaerythritol and 20 ml of tetrahydrofuran. To this was added 9.0 g (0.05 mole) methylphenyl methylamino silazane. The solution was refluxed for 5 hours; then the solvent was distilled leaving 7.2 g of a yellow, sticky liquid.

A small amount of the yellow, sticky liquid was placed in a 5-ml Teflon beaker and heated 138 hours at 190°C. The product was a resilient polymer, which became very friable after being heated at 400°C for 1 hour.

Attempts to form coatings on aluminum produced smooth, brittle films with poor adhesion.

2. Reaction of methylphenyl methylamino silazane with anhydrous phloroglucinol

In a 50-ml, 3-neck flask equipped with a reflux condenser, thermometer, dropping funnel, and magnetic stirrer were placed 2.5 g (0.02 mole) of anhydrous phloroglucinol and 20 ml of tetrahydrofuran. The solution was stirred, and 5.4 g (0.03 mole) of methylphenyl methylamino silazane in 15 ml of tetrahydrofuran was added. When the addition was complete, the reaction mass was a soft, rubbery material that was not soluble in tetrahydrofuran, benzene, or acetone. The rubbery material, after being heated at 125°C for 10 minutes, became brittle. Further heating at 400°C for 2 minutes caused the polymer to become black and friable.

3. Reaction of methylphenyl methylamino silazane with hydroquinone and phloroglucinol

a. 100:1 mole ratio, hydroquinone to phloroglucinol

In a 100-ml, 3-neck flask equipped with reflux condenser, thermometer, dropping funnel, and magnetic stirrer were placed 3.3 g (0.03 mole) of recrystallized hydroquinone, 0.037 g (0.0003 mole) of anhydrous phloroglucinol, and 30 ml of tetrahydrofuran. To this solution was added 5.4 g (0.03 mole) of methylphenyl methylamino silazane dissolved in 20 ml of tetrahydrofuran. The solution was refluxed 5 hours. The solvent was distilled leaving 4.9 g of a yellow, viscous polymer. At this point the effect of the phloroglucinol was not apparent.

A 9:1 mixture of the yellow, viscous polymer and ethylenediamine-silazane formed a semi-solid rubbery material on heating 97 hours at 190°C. Additional heating at 350°C caused the polymer to become friable with no resilience. If phloroglucinol had not been present, the polymer would have been resilient, according to previous experience.

Attempts to make coatings were unsuccessful because of brittleness and poor adhesion to aluminum.

b. 10:1 mole ratio, hydroquinone to phloroglucinol

The method for the preparation of this compound was similar to that described in 3-a. above. The procedure differed in that 0.026 mole of hydroquinone and 0.0026 mole of phloroglucinol were used with the 0.03 mole of methylphenyl methylamino silazane. The solvent was distilled from the reaction product and 5.7 g of a cream-colored, sticky material was recovered.

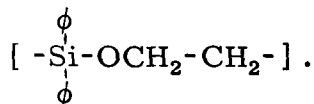
A mixture of the cream-colored, sticky polymer and ethylenediamine silazane in a 9:1 ratio was warmed 2 minutes at 190°C, and then removed from the oven and stirred. As the mixture cooled, it became a rubbery solid that crumbled easily, and the product could not be remelted at 350°C. This material became brittle after being heated at 350°C for 2 hours. Because of its poor strength, it was less promising than other materials that have better thermal stability.

Coatings on aluminum panels cracked and flaked on being heated at 350°C for 18 hours.

4. Reaction of hexaphenylcyclotrisilazane with ethylene glycol

a. 5% excess of glycol

In a 25-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser were placed 5.0 g (0.0084 mole) of hexaphenylcyclotrisilazane and 1.46 ml (1.64 g, 0.0265 mole) of recently distilled ethylene glycol. Heat was applied, and a homogeneous melt was formed when the temperature reached 220°C (about 35 minutes). After a total of 2.75 hours of heating, during which time the temperature rose gradually to 300°C, the product became too viscous to be stirred with a magnetic stirrer. On cooling the product formed a tan, transparent, tacky material, similar to the product obtained from equivalent amounts of hexaphenylcyclotrisilazane and ethylene glycol. The product weighed 5.54 g. This represents a 91% yield, if the product is assumed to be



A small amount of the tan material was placed in a 10-ml Teflon beaker and heated at 175°C for 2 hours. The polymer was soft but did not flow at this temperature. On cooling, it formed a non-tacky, flexible material that was fairly tough, but it could be pulled apart easily with the fingers. On further heating for a total of 17.5 hours at 175°C, the sample became softer. When cool, the polymer was less tough than it was initially. It was still soluble in benzene. Coatings on aluminum panels prepared from 10% benzene solutions of the samples heated for 2 hours and for 17.5 hours were unaffected by 19% hydrochloric acid on the flat surfaces after being heated at 400°C for 18 hours. However, the coatings did not protect the aluminum where the panels were bent.

b. With 5% excess hexaphenylcyclotrisilazane

In a 25-ml, 3-neck, round-bottom flask equipped with a magnetic stirrer, reflux condenser, and thermometer were placed 1.39 ml (1.56 g, 0.0252 mole) of ethylene glycol and 5.25 g (0.0088 mole) of hexaphenylcyclotrisilazane. Heat was applied, and a homogeneous melt was obtained when the temperature reached 190°C (about 50 minutes). The temperature was increased until it reached 260°C after 1.25 hour of heating. The mixture did not increase in viscosity in 2.5 hours at this temperature. The temperature was then increased to 360°C for 2 hours. Again there was no apparent increase in viscosity even though the product became darker in color. The temperature was increased to 386°C for 0.75 hour. The mixture was then a dark brown liquid that refluxed at this temperature, and the odor of escaping ammonia was detected. As the product cooled, it solidified to a dark brown, elastic, tacky solid at 150°C. This product weighed 6.10 g. The theoretical yield was 6.11 g, based on

$$\begin{array}{c} \phi \\ | \\ -\text{Si}-\text{OCH}_2-\text{CH}_2- \\ | \\ \phi \end{array} \text{ as the formula.}$$

A small amount of the brown, elastic solid was heated at 175°C for 5 hours in air in an effort to reduce the tackiness. It remained liquid at 175°C. On cooling, it formed a non-tacky, flexible material that could be stretched to a transparent film about twice the size of the original. On further heating for 63.5 hours at 175°C, the sample became more elastic but less tough. If pulled slowly a 1-inch sample could be stretched about 2 feet.

Coatings were prepared on aluminum from a 10% benzene solution of the elastomer that had been heated for 68.5 hours. After being heated at 400°C for 18 hours, the panels were bent and immersed in 19% hydrochloric acid. Except for a few pinholes, the aluminum was unaffected by the acid in the coated areas.

c. With 5% glycerol

In a 25-ml, 3-neck, round-bottom flask equipped with a thermometer, reflux condenser, and boiling chip were placed 5.0 g (0.0084 mole) of hexaphenylcyclotrisilazane, 1.39 ml (1.56 g, 0.0252 mole) of ethylene glycol, and 0.10 ml (0.12 g, 0.0013 mole) of recently distilled glycerol. Heat was applied, and in 20 minutes, when the temperature reached 180°C, the melt became homogeneous. The viscosity increased noticeably as the temperature rose. The melt became too viscous for stirring in 1.25 hour when the temperature reached 332°C. When cool, the product was 5.88 g of a transparent, tan, tacky solid. A small amount of this material heated in a 10-ml Teflon beaker at 175°C for 2 hours remained soft and tacky; it cooled to an elastic disc which was tougher than those formed from the other reactions of hexaphenylcyclotrisilazane with ethylene glycol. The polymer's thermal stability was appraised by heating a small piece of the disc at 400°C. After being heated 10 minutes and then cooled, the sample was brittle in the thinner places; after heating 20 minutes, the whole sample crumbled on cooling. Another portion of the disc heated at 350°C for 30 minutes remained liquid while hot and was still flexible when cool, but it had little strength. After 45 minutes at 350°C, the sample crumbled on cooling.

Coatings were made by dissolving the tan, tacky solid to form a 10% solution in benzene and spreading the solution on aluminum. After being heated at 400°C for 18 hours, the panel was bent and immersed in 19% hydrochloric acid. The coating remained intact, except where it was bent.

IV. POLYMERS MADE FROM METHYLPHENYL SILYLAMINES BY SELF-CONDENSATION AND BY HEATING IN AIR

A. Discussion

Silylamines made from methylphenyldichlorosilane have been studied previously with results as summarized in Report 32, page 29, and Report 35, page 17. The methyl group was previously found to impart some flexibility to the polymers, and some have had outstanding thermal stability for flexible and resilient materials. Investigation of these polymers has been continued in the past month in an effort to increase the toughness of types of materials previously made.

The most encouraging new polymers have resulted from the use of triethylamine in the reaction of methylphenyldichlorosilane with ammonia. An initial product was produced that was a viscous liquid without the small amount of crystalline material that is normally obtained in a reaction with no triethylamine. Evidently cyclization was inhibited and polymerization was enhanced. The benefit of triethylamine was apparent, because the methylphenyl silazane made with it could be made into tougher coatings and elastomers than any that had been made previously. For ease of discussion, the new material will be called "methylphenyl silazane-triethylamine." Coatings 6-8 mils thick on aluminum made with methylphenyl silazane-triethylamine and no other material remained in place for 5 hours at 400°C. A mixture of the methylphenyl silazane-triethylamine with ethylenediamine silazane was cured to a flexible resilient sheet that remained flexible for 4.5 hours at 400°C. The time limit for retention of resilience at 400°C has not been determined. This resilient polymer was considerably tougher than the one described in Report 32, page 29, and Report 35, page 17, but it was much more easily torn than Viton A and silicone rubbers.

B. Experimental Details

1. Reaction of methylphenyldichlorosilane with ammonia in the presence of triethylamine

In a 1-liter, 3-neck flask equipped with stirrer, reflux condenser, thermometer, and gas inlet tube were placed 95.5 g (0.5 mole) of methylphenyldichlorosilane, 101.2 g (1.0 mole) of purified triethylamine, and 600 ml of benzene. The solution was stirred for 30 minutes. Ammonia, after being dried over sodium, was passed over the stirred solution for 4 hours. The temperature was kept below 25°C during the addition. After the addition of the ammonia the reaction was refluxed for 3 hours. The salt was filtered off, and the benzene and triethylamine were distilled from the reaction. The product was 66.7 g of a cloudy, viscous liquid. This liquid is being called methylphenyl silazane-triethylamine

2. Properties as a coating on aluminum

Methylphenyl silazane-triethylamine was boiled in a test tube for 8-10 minutes during which time it became a very viscous, sticky liquid. This was applied to an aluminum panel and heated at 400°C for 5 hours without cracking or discoloration; however, after longer heating at this temperature, the coating crazed when the panel was bent. The best time and temperature for curing have not been determined. The coating did not become hard in 19 hours at 190°C. However, heating for 3 hours at 350°C produced a hard, transparent, pale yellow film that adhered well to the aluminum. The hardness, color retention, thickness, and excellent adhesion of this film make the methylphenyl silazane-triethylamine of considerable interest as a coating agent.

3. Properties of product formed with ethylenediamine silazane

A mixture of the boiled methylphenyl silazane-triethylamine and ethylenediamine silazane in a 9:1 ratio cured to a tacky rubbery solid in 4 days at 190°C. Heating at 400°C for an hour removed the tackiness. This rubbery material remained flexible and had fair strength after being heated at 400°C for 4.5 hours. At the same temperature Viton A remains resilient for about 30 minutes.

V. REACTIONS OF ETHYLENEDIAMINE SILAZANE

A. Discussion

Ethylenediamine silazane, a pale yellow viscous liquid that is the product of the reaction of ethylenediamine and dimethyldichlorosilane, is presently being investigated to find a means of improving it for several purposes. It now appears that treatment of EDS with bis(methylamino)-diphenylsilane has some merit. EDS has been used in this program to increase the flexibility and curability of other silazane materials in coatings and resilient polymers. It provides good thermal stability and elasticity but it has not been very promising when used alone in any applications because of low strength. Recently, several attempts have been made to improve EDS, either for use alone or with other materials. Some of the attempts were slightly beneficial, but none of the improvement was of sufficient magnitude to make EDS attractive for use alone. On the other hand, the treatment of EDS with bis(methylamino)diphenylsilane seems to have resulted in a worthwhile improvement in the ability of EDS to combine with the by-product of hexaphenylcyclotrisilazane to form coatings. Inasmuch as coatings made with EDS and by-product have considerable potential utility, this could be an important development. It will be investigated further to determine the effects of the treatment with bis(methylamino)diphenylsilane on curing conditions, flexibility, and thermal stability of the coatings.

Reactions of EDS with small amounts of ethylene oxide, hydroquinone, Epon 828 (an epoxide starting material for epoxy polymers), and silicon tetrafluoride were disappointing. Although some reaction occurred between EDS and the epoxides, coatings made from the products were not homogeneous, and no promising leads to useful materials were found. When EDS was treated with silicon tetrafluoride, moisture-sensitive liquids, gels, and powders were formed. Treatment of EDS with hydroquinone led to a polymer that was slow in curing and that was brittle when cured.

Addition of triethylamine in a preparation of EDS seemed to increase the toughness of films subsequently prepared from the product by a barely perceptible amount. This possible improvement will be checked further in connection with films made from the hexaphenylcyclotrisilazane by-product.

B. Experimental Details

The amount of replaceable hydrogen in EDS was not known, and so a method of calculating equivalence based on silicon was adopted. The approximate amount of silicon in EDS was known by analysis.³

1. The reaction of EDS with bis(methylamino)diphenylsilane

Two reactions of EDS with bis(methylamino)diphenylsilane were described in the preceding report, pages 11-12. Coatings made from the product of the reaction were much like coatings made with untreated EDS except that they were slightly tougher. However, they could be scratched easily with the fingernail.

Coatings were also made from the product of the EDS-bis(methylamino)diphenylsilane reaction by mixing it with the by-product obtained in the preparation of hexaphenylcyclotrisilazane.⁴ The by-product, 9 parts, and the material obtained by heating EDS with 7% of the equivalent weight of bis(methylamino)diphenylsilane, 1 part, were dissolved in benzene to form a 10% solution. The solution was spread on aluminum, the benzene was evaporated, and the residual film was heated at 190°C for 45 hours. The coating produced was shiny, transparent, and hard. The coating protected the aluminum from 19% hydrochloric acid even when it had been bent after heating. A similar coating made with untreated EDS and the by-product cracked at the bend. These coatings will be investigated further at higher temperatures.

The material obtained from the reaction of EDS with bis(methylamino)diphenylsilane (7% of the equivalent weight) was stirred with 10% by weight of Epon 828 (Shell Chemical Company). The mixture was spread on an aluminum panel and heated 1.7 hour at 126°C and 1.0 hour at 300°C. The coating was tough, glossy, and unwrinkled, but it became sticky on standing in the laboratory air for 30 minutes.

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3. Annual Summary Report, Contract NAS8-1510, George C Marshall Space Flight Center, February 28, 1962, page 85, paragraph 1, and analysis, p. 81, column 1.
 4. Annual Summary Report, Contract NAS8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 58-60 and 61-64.

2. The reaction of EDS with Epon 828

a. Reaction of EDS with 1% by weight of Epon 828

EDS, 9.9 g (0.101 g atoms of silicon), and Epon 828, 0.1 g, obtained from Shell Chemical Company were mixed in a 25-ml, round-bottom flask equipped with a thermometer, magnetic stirrer, and reflux condenser. The mixture was heated slowly up to 155°C and held at this temperature for 1.0 hour. It was then heated at 210°C for 1.0 hour. The temperature was increased in 30 minutes to 270°C. The product was a dark brown semi-solid flecked with lumps of a white solid. Efforts to dissolve the white solid by heating and with solvents such as benzene, dioxane, and tetrahydrofuran were unsuccessful. The preparation of coatings was not attempted because of the non-homogeneity of the product.

b. Reaction of EDS with 10% by weight Epon 828 in dioxane solution

EDS, 9.0 g (0.092 g atoms of silicon) was dissolved in 12.0 g of purified dioxane in a 50-ml, round-bottom flask equipped with a reflux condenser, thermometer, and magnetic stirrer. Epon 828, 1.0 g, was dissolved in 10 ml of purified dioxane and added drop-wise. The mixture was stirred for 1 hour, and then heated to 60°C for 1 hour.

The dioxane was distilled off. Heat was applied until the temperature went to 310°C and the product became solid. When coatings were made from the product the film separated into hard and soft portions. Evidently dispersion of the Epon 828 had not been complete.

3. Reactions of EDS with hydroquinone

a. Equal weights of EDS and hydroquinone

EDS, 7.59 g (0.078 g atoms of silicon), was treated with a solution of hydroquinone, 7.48 g (0.0679 mole), in 20 ml of tetrahydrofuran in a 100-ml, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser. The temperature rose 16°C, and the brown solution in the flask turned white.

The solution was refluxed for 2 hours at 75°C, then the tetrahydrofuran was distilled off. The temperature of the reaction product was increased gradually for 5.75 hours to a final temperature of 280°C. The product was a dark brown, sticky, viscous liquid. Coatings made with the product cracked when bent and were easily scratched with a fingernail.

b. 1% by weight of hydroquinone

Hydroquinone, 0.1 g (0.0009 mole), was dissolved in 10 ml of tetrahydrofuran and added drop-wise to EDS, 9.9 g (0.10 g atoms of silicon), dissolved in 10 ml of tetrahydrofuran in a 50-ml, round-bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser. The temperature rose 11°C during addition of the hydroquinone solution. After the mixture had refluxed at 70°C for 2 hours, the tetrahydrofuran was distilled off. The temperature of the reaction product was increased gradually over 2.5 hours, from 70°C to 220°C. The product was more viscous than the original EDS resin. It was a light brown, sticky, viscous liquid. Coatings made with the product cracked when cooled and could be scratched easily.

4. Preparation of EDS in presence of triethylamine

Previous success with the use of triethylamine in the reaction of silicon halides with amines prompted its use in the preparation of EDS.

Dimethyldichlorosilane, 64.52 g (0.5 mole), was dissolved in 750 ml of anhydrous benzene in a 2-liter, round-bottom flask, equipped with a reflux condenser, mechanical stirrer, and dropping funnel. Triethylamine, 101.2 g (1.0 mole), was added to the benzene solution drop-wise with stirring. The mixture was stirred vigorously for 4 hours, and then ethylenediamine, 150.25 g (2.5 mole), was added drop-wise while stirring was continued.

The reaction mixture was refluxed at 80°C for 4 hours. Then the benzene layer was separated from the oily layer and the benzene was removed at reduced pressure. The product was a yellow, viscous liquid. Coatings made from the product were slightly tougher than those made with EDS prepared without triethylamine, but they were quite soft and easily scratched.

5. Reaction of EDS with silicon tetrafluoride

Previous work on the addition of silicon tetrafluoride to hexamethylcyclotrisilazane produced a vitreous material of exceptional thermal stability.⁵ This reaction prompted attempts to bring about a more favorable reaction with EDS. EDS, 10.3 g (0.106 mole), was dissolved in 100 ml of anhydrous benzene in a 300-ml, round-bottom flask equipped with a reflux condenser, a thermometer, and gas inlet tube. A cylinder of silicon tetrafluoride was attached directly to the reaction flask with a rubber tube, and the flow of gas into the reaction flask was regulated so that it kept a balloon, attached to the top of the reflux condenser, inflated. The positive pressure of silicon tetrafluoride was maintained for 1.5 hours. For the last 0.5 hour no silicon tetrafluoride was admitted, and there was no apparent change in the size of the balloon. The weight of silicon tetrafluoride that reacted was 2.65 g (0.0254 mole).

The mixture was heated slowly; and when the temperature reached 50°C, white flakes of solid appeared in the clear solution. The temperature was increased to 80°C and the solution was refluxed at that temperature for 3 hours. Samples removed from the flask and exposed to air turned cloudy immediately and dried to a white powdery solid. The benzene was drawn off leaving in the reaction flask a gel with flakes of crystalline solid. On heating about a gram of the product at 260°C for 1.5 hours, it turned dark black and became a very brittle solid. Thus the reaction of silicon tetrafluoride with EDS appears to be less encouraging than the reaction of silicon tetrafluoride with hexamethylcyclotrisilazane.

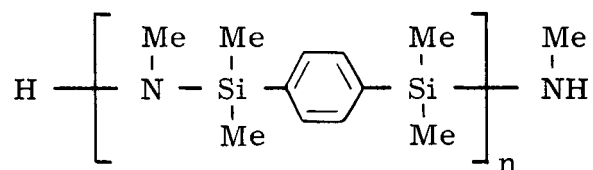
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5. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, February 28, 1962, pages 34-37.

VI. SILICON-NITROGEN POLYMERS CONTAINING AROMATIC BRIDGES

A. Discussion

Work on the silicon-nitrogen polymers with phenylene bridges has been continued with the objectives of duplicating or improving the first results and of studying the effect of several variants of the processing conditions.

Our first preparation of a polymer with phenylene bridges between Si-N-Si units (Polymer 3205-55-4) was described in Report 32, page 25. Subsequent repetitions failed to produce polymers with equal toughness, as discussed in the preceding report, page 13. In the past month, however, efforts to modify the prepolymer before curing it in air have essentially resulted in reproducing cured polymers with the toughness of 3205-55-4. It appears that the prepolymer, which is obtained by the reaction of methylamine with 1,4-bis(dimethylchlorosilyl)benzene, polymerizes further on standing or on being heated and thus produces a stronger polymer when cured. Meticulous efforts to improve the purity in each reaction subsequent to the first apparently resulted in lower molecular weight products from the reaction between 1,4-bis(dimethylchlorosilyl)-benzene and methylamine. This product has been called the prepolymer because it evidently is a mixture represented by the following formula:



In the first preparation, the molecular weight of the prepolymer was about 730 which suggested that n was 3 to 4. In subsequent preparations, the viscosities of the products were lower, but their molecular weights have not been determined.

The heating schedule during curing in air affects the toughness of the final polymer. When the preceding report was written, we were attempting to cure the prepolymer by heating at 250°C for 16 hours, as we did for the first preparation. The cured polymers were quite flexible but relatively weak. In the past month, we found that the same prepolymer heated for 120 hours at 200°C and then 24 hours at 250°C formed a fairly tough highly elastic polymer that crystallized on standing for an hour at room temperature. After crystallization, the toughness was increased and elasticity was decreased. Elasticity returned with heating above 100°C. Some resilience remained in the polymer after heating at 400°C for 30 minutes, but the polymer did not retain resilience as long at 400°C as the one described in Section IV-A. and IV-B-3. of this report.

Recently it was found that the original polymer with the desirable toughness is soluble in tetrahydrofuran and that it has a molecular weight of 110,000, as determined by light scattering. Thus, it may be possible to make films, and possibly fibers, from solutions of it.

Attempts to polymerize the prepolymer by heating it at 200°C under reduced pressure caused a decided increase in viscosity. Attempts to cure the resulting material at 250°C for 24 hours did not reproduce the desired toughness of sample 3205-55-4. There was some evidence that the curing rate was slightly faster than that of the untreated prepolymer, but the improvement was not sufficient to be of practical significance.

Because meticulous purification of 1,4-bis(dimethylchlorosilyl)benzene seemed to have an undesirable effect in one experiment, a sample of the compound was treated with a small amount of water before reaction with methylamine. The product from the reaction was cured at 250°C for 48 hours to produce an elastomer much like 3205-55-4. It was slightly tacky and very elastic when removed from the oven, and then it crystallized on standing to form a tough, flexible polymer. This procedure may have merit and will be evaluated further.

The variable results emphasize the importance of further studies to determine what factors influence toughness.

B. Experimental Details

1. Preparation of 1,4-bis(dimethylchlorosilyl)benzene

The most recent preparation of 1,4-bis(dimethylchlorosilyl)benzene was the fifth that we have made. The procedure and conditions used were essentially the same as described in Report 32, pages 23-24. The only exceptions were that a double-size batch was made and the final product was distilled only once at reduced pressure. The final retained fraction of 114 g had these characteristics: b. p. 118-128°C at 1.7 mm pressure; white crystals; neutral equivalent, 147 (theory, 131.7). These characteristics closely resemble those of the 1,4-bis compound that was used in the preparation of the first polymer with phenylene bridges (Report 32, page 25).

2. Reaction of 1,4-bis(dimethylchlorosilyl)benzene with methylamine after pretreatment with heat

The reaction of 1,4-bis(dimethylchlorosilyl)benzene with methylamine to form the pre-polymer was carried out as described in Report 32, pages 24-25. Before the final polymerization, the pre-polymer was heated at 200°C for 24 hours at a pressure of 0.5 mm. After this treatment, the product was liquid at 200°C, but it became a solid on cooling to room temperature. This product was heated in air at 250°C for a total of 16 hours. At the end of 30 minutes, a film had formed on the surface of the liquid; and, at the end of an additional 2 hours, the mass had become a highly viscous liquid. At the end of 16 hours, a tacky, amber colored, elastic solid had formed. The curing in this experiment differed from the curing of pre-polymer that had not been heated at reduced pressure in that the latter required 8 to 10 hours for a film to form. In both cases, heating at 250°C for 48 hours was necessary to produce the elastomeric final product, and neither was as tough as polymer 3205-55-4.

3. Reaction of 1,4-bis(dimethylchlorosilyl)benzene with water and then with methylamine

1,4-Bis(dimethylchlorosilyl)benzene, 9.0 g (0.03 mole), was dissolved in benzene, 200 ml, and 0.05 g (0.003 mole) of water was added. After stirring for 1 hour at room temperature, small droplets remained visible in the mixture. On raising the temperature to 80°C, all the droplets disappeared in 5 minutes. Methylamine was then added in excess as in Report 32, page 24. After the benzene was distilled off, the clear, yellow, viscous product weighed 7.0 g. It was less viscous and less cloudy than products made similarly, but without the water.

The methylamino product made with water was cured at 250°C for 48 hours to form a highly elastic, slightly tacky solid. When left at room temperature for an hour, it crystallized and was tough and flexible but not elastic. The properties were similar to those described in Report 32.

VII. THE INFLUENCE OF TERTIARY AMINES ON THE AMINE-SILICON HALIDE REACTION

A. Discussion

Triethylamine has been found to be beneficial in preventing cyclization in reactions of chlorosilanes with amines. The preceding quarterly report (Report 35, page 26) described the role of triethylamine in the reaction of diphenyldichlorosilane with ammonia to produce a material in 90-95% yields that served as an excellent coating agent. Without triethylamine the agent was obtained only in 17% yield. In the past month, the reaction was studied further at low and high temperatures. At a low temperature, 1-10°C, the reaction proceeded in about the same way that it does at 25-55°C with no attempt to control the temperature. At a high temperature, 125-143°C, with tributylamine, the yield of crystalline material was about 20%, which showed that an appreciable amount of cyclization had occurred. Polymers of high molecular weight were not produced.

B. Experimental Details

1. Reaction at ordinary temperature

Recently distilled diphenyldichlorosilane, 28.90 ml (35.32 g, 0.139 mole) was added to 39.05 ml (28.23 g, 0.279 mole) of triethylamine in 300 ml of benzene. The mixture was slightly cloudy. It was stirred while dry ammonia was passed over the surface for 5 hours. The temperature rose to 55°C. The solution was allowed to stand overnight, then it was centrifuged to remove the salt, and the benzene was distilled off, finally at reduced pressure. The product was 25.0 g of a tan, slightly viscous liquid. This represents 91% yield if the formula is assumed to be $-\text{SiPh}_2\text{NH}-$.

A coating was made with the product by spreading 0.2 ml of a 10% solution in benzene over an area of about 12 square centimeters on an aluminum panel. The panel was heated 18 hours at 400°C. Then it was bent and placed in 19% hydrochloric acid. The coated area had small pinholes in it indicating that the coating was extremely thin, but there was no evidence of cracking at the bend.

2. Reaction at low temperature

The reaction at low temperature was run with the same materials as the reaction at ordinary temperature except that the solvent was toluene. The addition of ammonia was started with the solution at 1°C, and the temperature was allowed to rise to 10°C. In 30 minutes, the reaction rate had decreased, and the temperature was held at 2°C for 1.75 hours. The mixture was allowed to stand overnight at room temperature under an atmosphere of ammonia as maintained by a balloon, then it was warmed to 90°C to boil off the ammonia. The resulting solution was filtered, and the toluene was distilled. The product was a cloudy, colorless, viscous liquid that weighed 25.1 g. The yield was 91% of theory, assuming the formula to be $-\text{SiPh}_2\text{NH}-$. A coating made in the manner of the one described in the preceding paragraph performed the same.

3. Reaction at elevated temperature

Recently distilled diphenyldichlorosilane, 28.90 ml (35.32 g, 0.139 mole) was added with stirring to 300 ml (233.5 g, 1.26 mole) of tri-n-butylamine that had been distilled from phthalic anhydride and then from potassium hydroxide. The solution was cloudy. Heat was applied, and at 115°C the cloudiness disappeared. At 136°C, ammonia was introduced, and the temperature rose to 143°C. In 30 minutes, the temperature dropped to 125°C, and then heat was applied to keep it at 125°C for 3 hours while the atmosphere of ammonia was maintained. The mixture was allowed to stand overnight under an atmosphere of ammonia. The product was isolated by centrifugation and distillation of the tributylamine at reduced pressure. The product was a white, semi-crystalline, viscous mixture. The crystalline portion, 5.01 g, was separated by dissolving the viscous liquid in Skellysolve "B". The crystals melted over a range of 189-215°C. Evidently they were crude hexaphenylcyclotrisilazane, obtained in 20.5% yield. A coating made with the non-crystalline product in the manner described in Section 1 above, crazed in the bent areas.

VIII. ANTICIPATED WORK

The work on silicon-nitrogen polymers with phenylene bridges in the main chain will be continued in an effort to prepare samples that will demonstrate their potential for high-temperature gaskets and sealants. Polymerization with heat and peroxides will be tried and the effect of silica will be determined.

Studies of methods of silylating polyethylenimine that are in progress will be continued. Polyethylenimine is a polymer of high molecular weight, and successful silylation could produce a polymer with high molecular weight and excellent thermal stability.

Studies of the reaction of phthalocyaninodichlorosilane with ammonia will also be continued. The starting material has been made.

Methylhydrogendichlorosilane will be treated with ammonia and methylamine in the presence of triethylamine in an effort to make an additive for silazanes that will promote curing at low temperatures.

The reaction of bis(methylamino)diphenylsilane with aluminum hydroxide will be investigated further as a possible route to thermosetting polymers of high thermal stability.

Some brief studies of the polymerization of nonamethylcyclotri-silazane in the presence of tributylamine are being conducted in an effort to obtain more data on tertiary amines as agents for ring-opening and chain extension. If successful, these experiments would produce a fully methylated silicon-nitrogen polymer of exceptional thermal stability.

IX. TIME EXPENDITURE

The time expenditure during the monthly period covered by this report (February) was 1144 man hours.

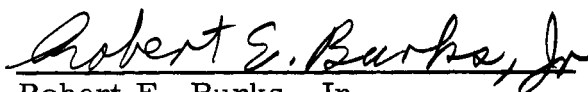
ACKNOWLEDGMENTS

Mr. Robert E. Lacey, Senior Chemical Engineer, has assisted with the planning and interpretation of the laboratory work. Miss Mary Ann Fromhold, Assistant Chemist; Mr. Charles L. Christy, Chemical Technician; Mrs. Ruth Ann Ratcliff, Assistant Chemical Engineer; and Mr. J. Fred Lyle, Associate Chemical Engineer, assisted with the laboratory work.

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Birmingham, Alabama

March 18, 1964

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PROGRAM PLANNING CHART

Allotted time, man-hours		1963												1964		
		April	May	June	July	August	September	October	November	December	January	February	March			
	A. Synthesis of Polymers and Compounds with Desired Characteristics															
	1. Lubricants - unsymmetrical derivatives of cyclic silazanes (see B. 1. b)			X	X	X										
400	2. Elastomers - silyl derivatives of ethylenediamine (see B. 7)		X	X	X	X										
400	3. Structural plastics															
900																
	B. Study of the Chemistry of Silicon-Nitrogen Compounds															
	1. Metalation of silylamines as a method of synthesis															
500	a. Polymers	X	X	X	X	X										
-	b. Lubricants (see A. 1)															
900	c. Organometallics							X	X	X	X					
	2. Polymerization of cyclic silazanes at high temperatures and pressures															
280	3. Condensation polymerization of silylamines with difunctional aromatic compounds			X	X											
280	4. Steric factors to inhibit cyclization															
900	5. Polyethylenimine as a source of silicon-nitrogen polymers							X	X	X	X					
400	6. Properties of methylhydrogen silazanes							X	X	X	X					
200	7. Elastomers from ethylenediamine silazanes (see A. 2)															
-	8. Addition of silicon tetrafluoride to silazanes and amines															
280	9. Heats of combustion as indicators of aromaticity															
420	10. Polymers from methyltrichlorosilane and silicon tetrachloride															
420	11. Silicon-nitrogen compounds with aromatic bridges															
510	12. Factors affecting hydrolytic and thermal stabilities	X	X	X	X	X		X	X	X	X					
510				continuous												
	C. Evaluation of Polymers (thermal, hydrolytic, and radiation stability)															
510	D. Applications - Search for New Uses															
	E. Heat Barriers															
510	F. Preparation of Final Report															
170																
9000																

Descriptions correspond to sections of Proposal 2186 - March 20, 1963.